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Chemical characteristics of basal ice near Hamna Icefall, East Antarctica

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Abstract: Debris-laden basal ice is exposed along an ice cliff (about 30 m high) near Hamna Icefall, Sôya Coast, East Antarctica. The basal ice about 6.8 m thick can be divided into an upper part (5.5 m) and a lower part (1.3 m) based on stratigraphic features. Major dissolved ions of the basal ice are probably composed of eight species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^- and HCO_3^-). Almost all Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- in the basal ice are considered to have originated from chemical erosion of rock minerals at the base of the ice sheet. According to a calculation of ion composition, the primary rock mineral dissolved in the basal ice is considered to be carbonate.

1. Introduction

Basal ice preserves physical and chemical signals of the conditions of its formation, and serves as an indicator of processes and environments that exist in the inaccessible subglacial zone (Knight, 1999). It is important to make clear chemical characteristics of basal ice, because they provide knowledge about formation processes (*e.g.* Souchez and Lorrain, 1978; Goodwin, 1993) and/or about mechanisms of chemical erosion (*e.g.* Brown *et al.*, 1996) at the inaccessible inland bases of ice sheets and glaciers.

The first study of major dissolved ions in basal ice was performed by Souchez *et al.* (1973), who determined the ratio of $(Na^+ + K^+)/(Mg^{2+} + Ca^{2+})$ in basal ice at Glacier d'Argentière, French Alps, as evidence of refreezing at the base of the glacier. Goodwin (1993) showed that the basal ice at Law Dome, Antarctica, was formed from basal freezing of desalinated sea water and an episodic mixture of basal meltwater and sea water, using co-isotopes and cations in the basal ice. Jansson *et al.* (1996) obtained field evidence for Lliboutry's (1993) regelation theory using cations and debris concentrations of the basal ice at Engabreen, northern Norway. As shown in these precedent studies, major dissolved ions in basal ice are effective parameters to make clear occurrences at the inaccessible inland bases of ice sheets and glaciers.

The present paper discusses chemical characteristics of the basal ice near Hamna Icefall, Queen Maud Land, East Antarctica (Fig. 1). The purpose of the present study is to make clear chemical characteristics of the Hamna basal ice using major dissolved

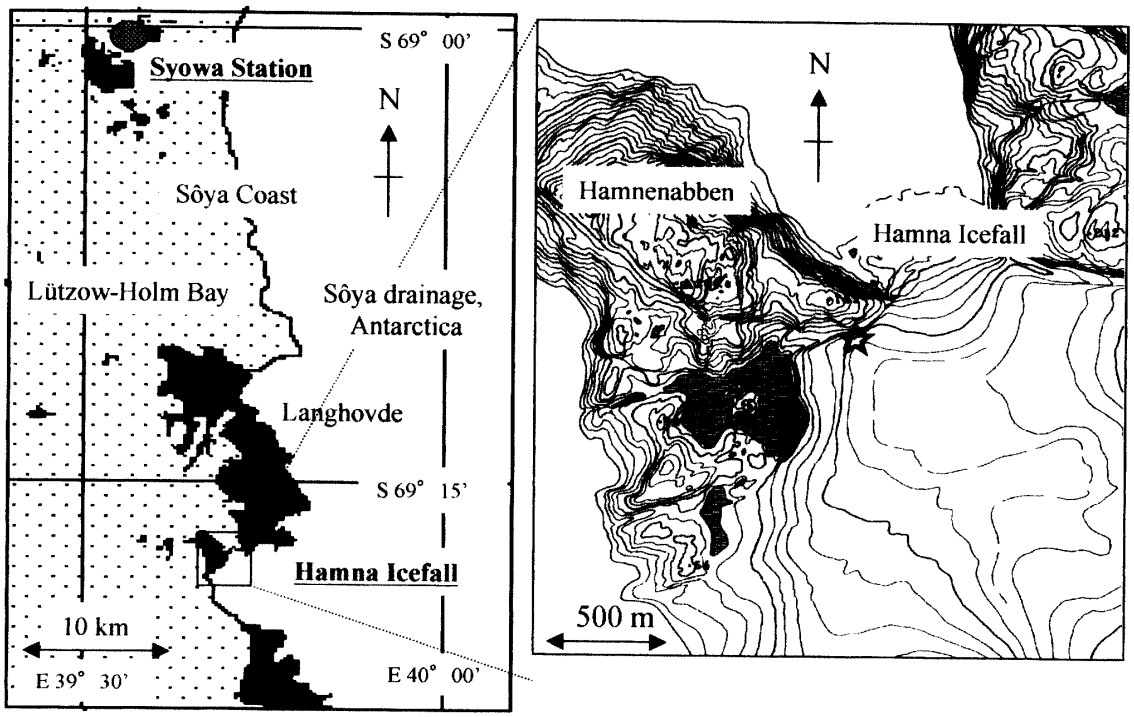

Fig. 1. Location maps of the Hamna basal ice, exposed at the east coast of the Sôya drainage in East Antarctica. The sampling site is shown by ☆ on the map.

ions, liquid electrical conductivity and pH in the basal ice.

2. Study site and analytical procedures

The sampling site for basal ice was selected at the left bank of Hamna Icefall, one of the outlet glaciers from the East Antarctic ice sheet 30 km south of Syowa Station, Sôya Coast, Queen Maud Land (Fig. 1). The Hamna basal ice is exposed along an ice cliff (about 30 m high) at the bank. The basal ice was sampled in winters 1994 and 1998 during the 35th and 39th Japanese Antarctic Research Expeditions. A columnar section was cut from the ice cliff (Fig. 2). It covers the lower 9 m of the cliff, so the sample includes not only the basal ice but the upper undisturbed ice sheet ice. The sample was transported frozen to cold laboratories in the Institute of Low Temperature Science and National Institute of Polar Research, and was preserved there at -20°C.

Laboratory analyses of the basal ice and the ice sheet ice were conducted. Items of the analyses are stratigraphy, debris concentration (% in wt), seven major dissolved ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and NO_3^-), liquid electrical conductivity (LEC) and pH. Analyses for major dissolved ions (MDI), pH and LEC were performed continuously with each sample thickness of 100 mm after the samples were filtered (pore size 0.45 μm). PH and LEC were measured by flow-cell-type sensors with the same method as Watanabe *et al.* (1997). Errors are estimated to be less than ± 0.01 for pH, $\pm 0.1\,\mu$S/cm for LEC ($\geqq 10\,\mu$S/cm) and $\pm 0.01\,\mu$S/cm for LEC ($<10\,\mu$S/cm). MDI was measured by ion chromatography with the same method as

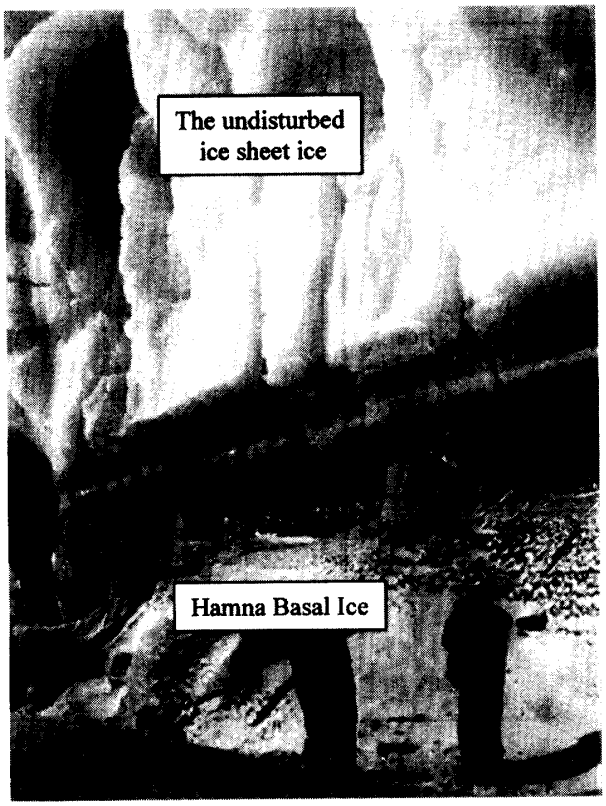

Fig. 2. Sampling site of the Hamna basal ice. This ice cliff is about 30 m high and debris-laden ice (=basal ice) is about 6.8 m thick. Dark-colored ice layers in the basal ice do not contain bubbles.

Igarashi *et al.* (1998). Errors are estimated to be less than 5% for each ion.

3. Results

In the first column from the left margin of Fig. 3, a stratigraphy of bubbly ice, bubble-free ice, and debris layers observed on the Hamna basal ice is shown. The figure also shows concentrations of debris, MDI, "Σ cations $-$ Σ anions", pH and LEC in ice. "Σ cations $-$ Σ anions" were calculated from,

$$\text{"}\Sigma\text{ cations} - \Sigma\text{ anions"}\ (\mu\text{eq/L}) = (H^+ + Na^+ + K^+ + Mg^{2+} + Ca^{2+}) - (Cl^- + NO_3^- + SO_4^{2-}). \quad (1)$$

The vertical axis of this figure represents depth measured downward from the boundary between the basal ice and the ice sheet ice above it. Hereafter, we take the depth in this way.

The Hamna basal ice about 6.8 m thick exhibits two peculiar stratigraphic features. One is the upper part of the basal ice (5.5 m in thickness), which consists of alternating layers of bubble-free and bubbly ice on the order of mm to cm in thickness and has low concentration (less than 1% in wt) of debris. The other is the lower part of the basal ice (1.3 m in thickness), which consists predominantly of bubble-free ice and has high concentration (less than 4% in wt) of debris.

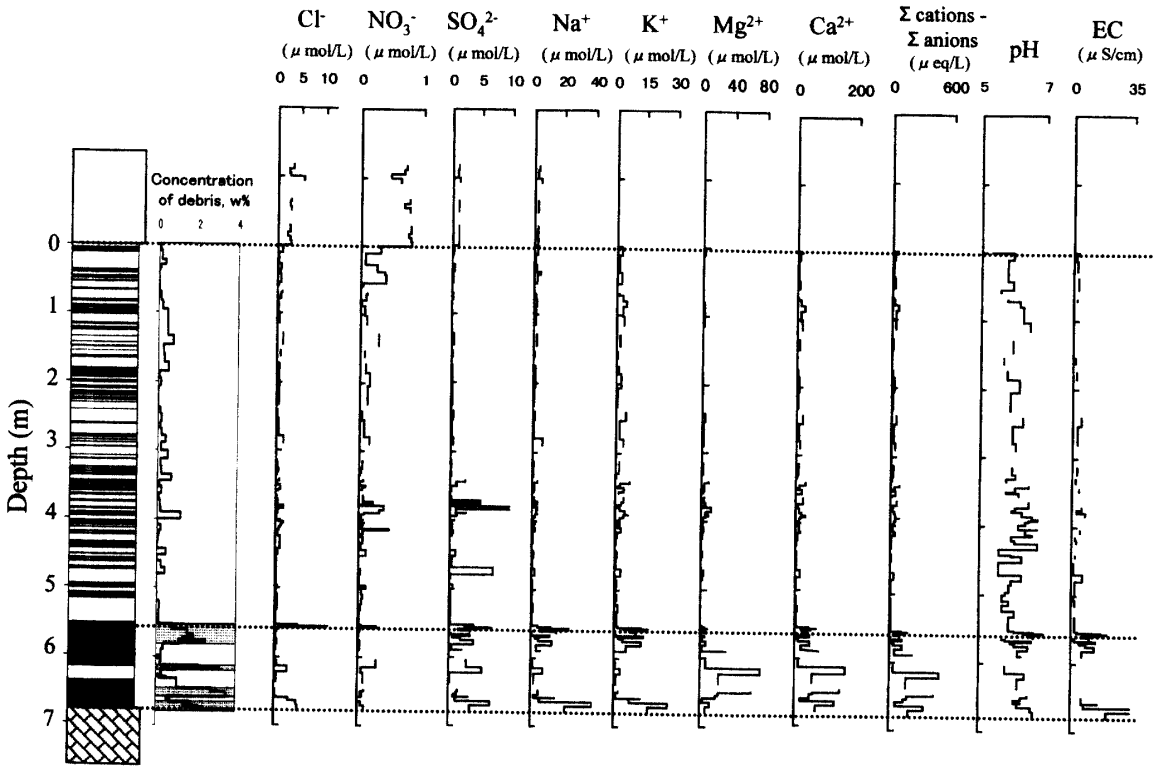

Fig. 3. Depth profiles of stratigraphy of bubbly ice, bubble-free ice, and debris layers observed on the Hamna basal ice, together with debris concentration in each layer, and seven MDI (μmol/l), Σ cations − Σ anions (μeq/l), pH and LEC (μS/cm) in ice. Bubbly ice is represented by open spaces and bubble-free ice by black spaces (first column). Debris layers shown by dotted spaces are composed of the bubble-free ice (second column). Dotted lines show interfaces between the ice sheet ice and the basal ice (0 m in depth), the upper part and the lower part of the basal ice (5.5 m in depth), and the basal ice and the base of the ice sheet (6.8 m in depth).

Values of pH in the basal ice range from 5.6 to 7.0, and are higher than pH in the ice sheet ice (=5.3). The larger pH of the basal ice is considered to be due to chemical weathering of rock minerals at the ice-bed interface (Tranter *et al.*, 1993). Values of LEC in the upper part of the basal ice are smaller than 10 μS/cm, whereas those in the lower part indicate 35 μS/cm for the maximum. MDI values in the ice sheet ice are composed mainly of Na^+ and Cl^-, both being 6 μmol/*l* at maximum. On the other hand, MDI in the basal ice is composed mainly of Ca^{2+} (160 μmol/*l* at maximum) and unmeasured anions associated with "Σ cations − Σ anions" (480 μeq/*l* at maximum).

4. Discussion

4. 1. Compositions of MDI in the Hamna basal ice

In Fig. 4, a relationship is shown by cross marks between measured LEC and calculated LEC. The calculated LEC values were estimated from concentrations of H^+ and seven measured ions and from values of theoretical electronic conductivity at

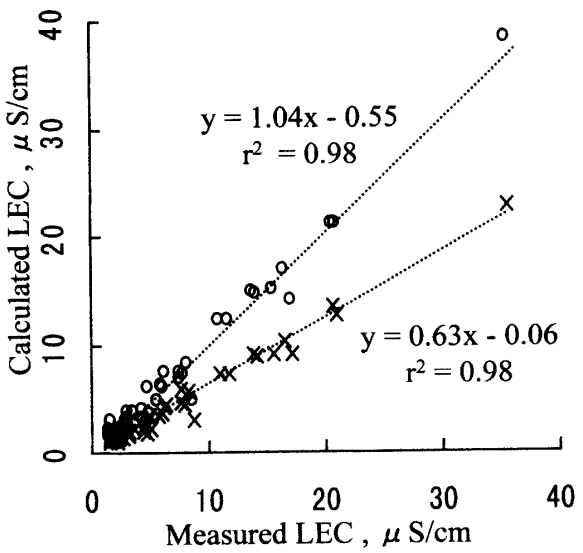

Fig. 4. Relationships between measured LEC and calculated LEC (×), and between measured LEC and another calculated LEC (○) taking account of HCO_3^-. The two dotted lines are approximate lines of the relationships.

infinite dilution. Although a high correlation coefficient ($r^2=0.98$) was obtained between the two LEC values, the measured LEC values are much larger than the calculated LEC values. The difference of these two is considered to be due to the contribution of anions with concentration equal to that of "Σ cations − Σ anions". Species of major anions in general river water are Cl^-, NO_3^-, SO_4^{2-} and HCO_3^- (Hirayama, 1992). From these considerations, we estimated that the concentration of "Σ cations − Σ anions" equals that of HCO_3^-. Figure 4 also shows a relationship by open circles between the measured LEC and another calculated LEC considering conductivity and concentration of HCO_3^-. A linear relation with a slope 1.04 and a correlation coefficient 0.98 was obtained. These results suggest that MDI in the Hamna basal ice is composed of eight ion species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^- and HCO_3^-), in particular Ca^{2+} and HCO_3^-. The ion balance in the Hamna basal ice is quite similar to that in general meltwater runoff from outlet glaciers in Antarctica (Watanuki, 1992). We could not carry out measurements for HCO_3^-, because of the small amount of samples of the basal ice which can not afford to analyze for titration.

4. 2. Origins of MDI and estimation of compositions of dissolved rock minerals

Table 1 shows average values of MDI, pH and LEC of the ice sheet ice, the upper part, the lower part of the basal ice and the whole Hamna basal ice. The sum of Na^+ and Cl^- concentrations in the ice sheet ice corresponds to 65.8% of the sum of seven ion concentrations (except for HCO_3^-). In the ice sheet ice, the correlation coefficient between Na^+ and Cl^- is 0.99, and the Cl^-/Na^+ (ppb) ratio (1.76) is in the good agreement with the ratio for sea salt (1.8). The ionic balance of the ice sheet ice is similar to that of snowpack in the middle and/or marginal parts of the Antarctic ice sheet (Kamiyama and Watanabe, 1994).

Sums of Ca^{2+} and HCO_3^- in the upper and the lower parts of the basal ice correspond to 83.1% and 83.6%, respectively, of sums of eight ion concentrations. Depth profiles of Mg^{2+}, Ca^{2+} and HCO_3^- (Σ cations − Σ anions) represent similar

Table 1. Average values of pH, eight MDI (μmol/l) and LEC (μS/cm) of the ice sheet ice, the upper part, the lower part of the basal ice, and the whole basal ice.

	pH	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	LEC
The ice sheet ice	5.3	2.78	0.72	0.98	2.44	0.15	0.31	0.55	—	—
The upper part	6.1	0.57	0.10	0.81	1.51	2.15	1.98	9.80	25.30	3.05
The lower part	6.3	2.35	0.07	2.66	9.49	7.46	11.83	46.45	125.76	10.79
The whole basal ice	6.2	1.15	0.09	1.42	4.13	3.89	5.21	21.91	58.18	6.61

Table 2. Percentage of calculated origins of MDI in the Hamna basal ice, following Sharp's method.

	1	2	3	4	5
Cl^-	100	0	0	0	0
NO_3^-	100	0	0	0	0
SO_4^{2-}	13.8	0	85.7	0	0
Na^+	24.0	0	0	76.0	0
K^+	0.6	0	0	99.4	0
Mg^{2+}	2.2	0	12.8	0	85.1
Ca^{2+}	0.1	0	8.1	0	91.8
HCO_3^-	0	1.5	2.1	12.0	84.4

1: Sea salt and snowpack. 2: Dissolution of atmospheric CO_2. 3: Coupled sulfide oxidation and carbonate dissolution. 4: Carbonation of aluminosilicate minerals. 5: Carbonation of carbonate minerals.

patterns to the profile of debris concentration (Fig. 3). It is also shown that concentration peaks of Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- in the lower part correspond to debris layers (Fig. 3). These results suggest that most of the Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- originated from the chemical erosion of rock minerals. Cl^- in general meltwater is considered to originate not from the chemical erosion of rock minerals but from a supraglacial source: *e.g.* sea-salt (*e.g.* Brown *et al.*, 1996). Since the ion balance in the Hamna basal ice is quite similar to that in general meltwater, it suggests that Cl^- in the Hamna basal ice originated from a supraglacial source.

We estimate compositions of dissolved rock minerals using the method established by Sharp *et al.* (1995). Table 2 shows calculated origins of MDI in the Hamna basal ice. The result indicates that more than 97% of K^+, Mg^{2+}, Ca^{2+} and HCO_3^-, 86% of SO_4^{2-}, and 76% of Na^+ originated from the chemical erosion of rock minerals. Particularly, 92% of Ca^{2+} and 84% of HCO_3^-, which are primary components of MDI, originated from the carbonation of carbonate. These results suggest that the primary component of rock minerals dissolved in the Hamna basal ice is carbonate, and imply that carbonate is one of the major components of rock minerals at the base of the Sôya drainage.

The average values of pH and HCO_3^- in the basal ice are 6.2 and 58.18 μmol/*l* (Table 1). The pressure of carbon dioxide (PCO_2) calculated from these two values at 25°C is 1.9×10^{-3} atm. The PCO_2 value is less than that with the $CaCO_3$-equilibriumed condition (6.7×10^{-1} atm at pH=6.2) and more than that with the CO_2-dissolved condition in pure water (1.9×10^{-5} atm at pH=6.2). This consideration suggests that

the Hamna basal ice contains some dissolutions from carbonate in non-equilibrium condition.

5. Concluding remarks

We have discussed chemical characteristics of the Hamna basal ice using MDI, pH and LEC values in ice. MDI of the Hamna basal ice is probably composed of eight ion species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^- and HCO_3^-). Sums of Ca^{2+} and HCO_3^- in the upper and the lower parts of the basal ice correspond to 83.1% and 83.6 %, respectively, of sums of eight ion concentrations.

Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and HCO_3^- in the Hamna basal ice originated mainly from the chemical erosion of rock minerals at the base of the ice sheet. It is estimated that more than 97% of K^+, Mg^{2+}, Ca^{2+} and HCO_3^-, 86% of SO_4^{2-} and 76% of Na^+ originated from the chemical erosion of rock minerals, and the primary rock mineral dissolved in the Hamna basal ice is considered to be carbonate. Further research on analysis of debris components would clarify the major components of rock minerals and extent of chemical erosion at the base of the Sôya drainage.

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